Faraday Discuss., 1997, **108**, 131–138

Direct detection and spectroscopy of O_4^*

Holly M. Bevsek, Musahid Ahmed, Darcy S. Peterka, F. Cortney Sailes and Arthur G. Suits*

Department of Chemistry, University of California, Berkeley and Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA

We have produced and directly detected a metastable state of tetraoxygen in a molecular beam, both by means of a dc discharge and by photodissociation of ozone in the collision region. The O_4^* produces a complex spectrum from which general conclusions may be made about its energetics and structure. The detection proceeds through a (1 + 1) resonant photoionization process in the vicinity of 300 nm, implying an energy for this species about 4 eV above that of two isolated O_2 molecules. A predominance of peak frequency differences in the range 411–419 cm^{-1} supports a cyclic D_{2d} geometry as predicted by *ab initio* calculations, although a definitive judgment on the structure of O_4^* awaits further study.

The existence of a stable, covalent O_4 molecule has been debated since Lewis first made this hypothesis in 1924.[1] Although the weakly bound dimer $(O_2)_2$ was identified in the 1960s,[2] the search continued for a cyclic structure that would have enhanced stability due to pairing of the two unpaired π^*_{2p} electrons in oxygen's highest occupied molecular orbital. The possibility of a metastable cyclic oxygen polymer is strengthened by considering the well known stability of sulfur rings. This system is also interesting since *c*-O_4 could be used as a high energy density material (HEDM) due to its energetic dissociation to two ground state O_2 molecules:

$$O_4 \rightarrow 2O_2\,; \qquad \Delta_r H = -48 \text{ kcal mol}^{-1}$$

based on the assumption[3] of normal O—O single bonds in O_4 and neglecting ring strain contributions.

The first theoretical attempt to determine whether a stable cyclotetraoxygen species exists was undertaken by Adamantides *et al.*[4] They found a minimum at the SCF-CI level in the potential surface for a D_{2d} geometry with approximately equal O—O bond lengths of *ca.* 1.4 Å, close to that of a normal O—O single bond. Calculations at a higher level of theory were later undertaken by Schaefer and co-workers,[3] confirming the D_{2d} geometry. Harmonic vibrational frequencies (see Table 1) were calculated along with the barrier to dissociation. This value was found to be about 6 kcal mol^{-1}, implying that O_4 is too unstable to be useful as a HEDM. Several other calculations[5–7] have been performed to determine whether a branched D_{3h} form of O_4 could exist. Such a state was found to exist approximately 2 eV above the D_{2d} geometry; however, it was also found to be unstable with respect to dissociation. A comparison of the various calculations on O_4 may be found in Fig. 1.

In spite of its instability, several attempts to produce O_4 have been made. Helm and Walter[9] have used charge transfer neutralization of O_4^+ to form O_4 in non-$(O_2)_2$ geometries; however, they only detected the O_2 dissociation products. Production of O_4

* Email: agsuits@lbl.gov

Table 1 Predicted harmonic vibrational frequencies for the D_{2d} geometry of O_4 from ref. 4

assignment	frequency/cm^{-1}	symmetry
ring stretch	877	A_1
ring deformation	783	B_1
O—O stretch	678	E
ring deformation	793	B_2
ring pucker	396	A_1

in non-dimer configurations was also performed by Continetti and co-workers[10] using the dissociative photodetachment technique with O_4^-. Again, only the O_2 dissociation products were observed, although they did not perform detection in the plane of the O_4^- beam. Recently, Jacox and co-workers[11] have attempted to produce *c*-O_n species by

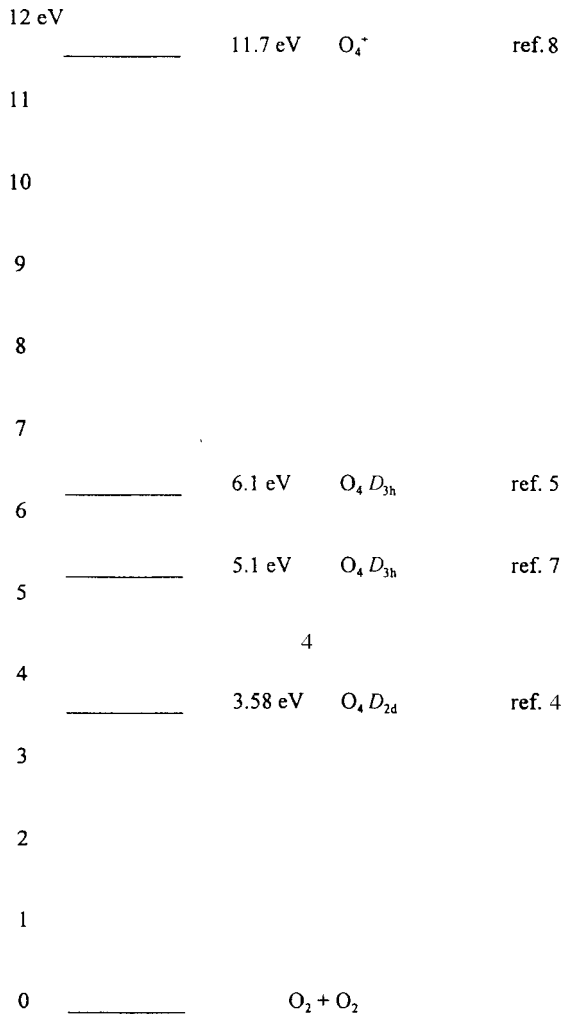

Fig. 1 Energetic comparison of several O_4 calculations

codepositing O_3 with $Ne^*(^3P_J)$ at 5 K. Although interesting species such as O_3^- and possibly an $O_2 \cdots O_4^+$ complex were observed, there was no evidence for formation of any *c*-O_n species. Recently, we have produced metastable O_4^* containing more than 4 eV above the energy of 2 O_2 molecules, consistent with predictions for *c*-O_4. A description of how we prepare this species and preliminary findings follow.

Experimental

A schematic diagram of the experiment is given in Fig. 2. Neat O_2 was passed through a Proch–Trickl[12] piezoelectric pulsed valve. The pulsed (200 μs) O_2 beam then passed through the center of two stainless steel electrodes, one at ground potential and the second at +3–5 kV. The ground plate was approximately 3 mm from the nozzle, and grounded to it. The pulse of O_2 between the electrodes produced an arc discharge which extended back to the nozzle orifice (as evidenced by widening of the orifice after many hours of use). The beam was then skimmed and travelled 6 cm where it was intersected by the unfocussed, frequency doubled output of a pulsed dye laser (Spectra-Physics, PDL-1) pumped by a Nd : YAG laser (Quantel, 592). The laser fluence was typically 1 mJ cm^{-2} or less. Resonance enhanced multi-photon ionization (REMPI) produced O_4^+ ions which were accelerated through a 20 cm time-of-flight tube. The ions struck a microchannel plate and the secondary electrons were accelerated towards a phosphor screen. The phosphorescence was detected by a photomultiplier tube, and the resulting voltage displayed on an oscilloscope. REMPI spectra were collected by passing the O_4^+ signal through a boxcar integrator and scanning the ionization wavelength.

Interestingly, we discovered that O_4^* was also produced when 5% O_3 seeded in He was photodissociated by focused 266 nm light at the nozzle of the pulsed valve. Replacing the ozone mixture with pure O_2 still produced O_4^*, but at approximately half the signal intensity. Spectra collected using this method of O_4^* preparation were identical in

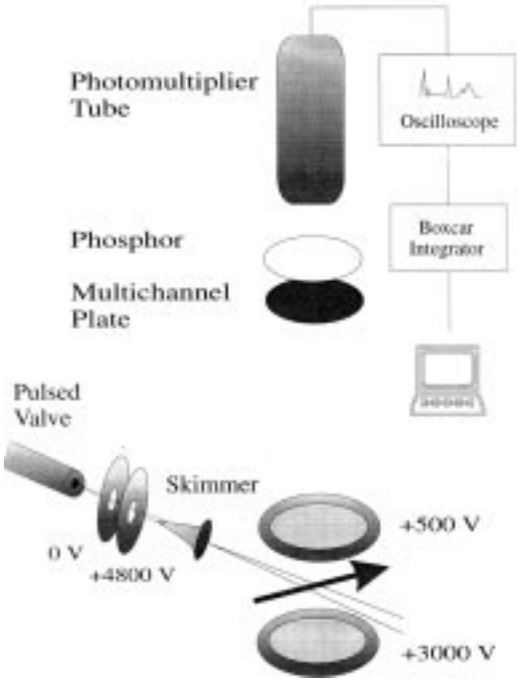

Fig. 2 Experimental schematic diagram

the spectral region scanned (300–315 nm) to those in which the O_4^* was formed with the discharge. Thus it appears that O_4^* is produced by ozone photodissociation in the environment of the supersonic expansion, providing a second pathway for the formation of O_4^*.

Results and Discussion

Typical time-of-flight mass spectra with the discharge on and off are displayed in Fig. 3. Mass calibration was performed using the O_2 signal visible in Fig. 3, and later by mixing He and Ar with O_2 and observing the non-resonant He* and Ar* signals. We have examined the region from 276 to 332 nm and these spectra, produced using a neat O_2 beam, are displayed in Fig. 4. This spectrum shows many intense peaks which are discussed in detail below.

A power dependence study was performed to investigate the energetics of this system; the results are shown in Fig. 5. The data are an average of the power dependence of four peaks in the 320–325 nm spectral region. Note the linear dependence which is obtained for the first three points, after which some saturation apparently occurs. A linear least-squares fit to the data prior to saturation (dashed line) yields a slope of 0.92, consistent with a (1 + 1)REMPI process with saturation of the ionization step. An overall linear fit to all of the data (solid line) yields a slope of 0.80. The spectrum in Fig. 3 allows us to make some general statements about the energetics of the initial and intermediate O_4^* states. The fact that we see vibrational structure out to 327 nm indicates that the initial state extends at least up to 4.1 eV above 2 O_2, while the intermediate state extends up to 7.9 eV. The evidence thus indicates that these spectra represent a metastable form of O_4 containing substantial internal energy relative to two O_2 molecules.

Alternative explanations for the intense O_4^+ spectra are not satisfying: possible candidates include higher polymers of oxygen that undergo dissociative ionization to give O_4^+. Although this explanation cannot be rejected absolutely, since there is no evidence to support the existence of higher oxygen polymers, the simpler explanation is preferred. Ions in the beam are deflected by the ion optics and do not survive into the probe

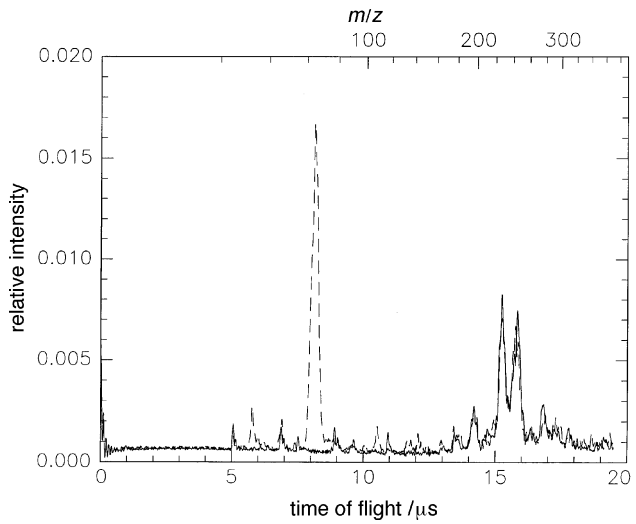

Fig. 3 Time-of-flight spectra from an O_2 molecular beam with the discharge on (dashed line) and off (solid line). Laser power is 1 mJ pulse^{-1} at 306 nm.

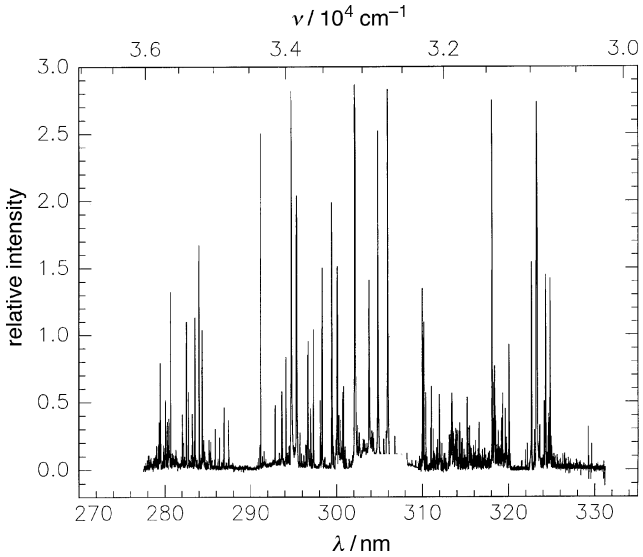

Fig. 4 (1 + 1)REMPI spectrum of O_4^* from 276 to 332 nm. Laser power is 800 μJ pulse^{-1}.

region, so they cannot account for the observed spectra. These spectra were not observed in beams in the absence of oxygen or ozone nor with the discharge off.

By assuming a typical peak velocity of the O_4^* beam to be 8×10^4 cm s^{-1} one can estimate a lower bound to the lifetime of 80 μs, although it may be much longer. These spectra imply both the existence of the metastable O_4^* and an excited intermediate state or states through which the resonant detection occurs. Furthermore, the narrowness of the spectral peaks indicates that the REMPI intermediate state must also have a relatively long lifetime, precluding strong predissociation of the intermediate state.

The spectrum is quite congested which is surprising considering the high symmetry expected for this system. Hot bands and combination bands are expected with a hot

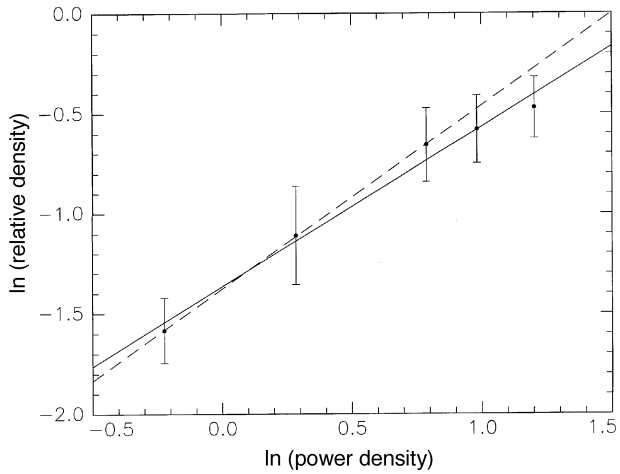

Fig. 5 Power dependence of four O_4^* peaks in the 320–325 nm spectral region. Solid line is a linear least-squares fit to the entire data set; dashed line is a linear least-squares fit to the first three points. Power density is measured in J cm^{-2} pulse^{-1}.

discharge source, although it is doubtful that all the peaks observed are due to excitations from only two or three fundamental frequencies. Deviations from the orbital-symmetry selection rules are known to occur when highly symmetric species undergo Jahn–Teller distortion,[13] and it is possible that this is the case with O_4^*. Furthermore, the geometry of the intermediate state or states is unknown and there could be as many as six excited vibrational modes, the maximum allowed for a tetra-atomic system. In light of this, we have measured the frequency difference between 99 peaks and looked for commonly occurring differences. Table 2 summarizes the peak-to-peak frequency differences along with their recurrence. There are naturally many other frequently occurring differences as would be expected with a total of 4851 peak differences; we chose to examine only those with 18 or more repetitions within the range $300 \leqslant \nu/\text{cm}^{-1} \leqslant 2000$ for simplicity. The conclusions we reach are therefore clearly tentative, and a more definitive discussion must await further studies.

Based on the 22 most commonly occurring frequency differences, we can make several observations. The two most often discovered differences are 437 and 801 cm^{-1} with 24 recurrences each. Together, the peaks comprising these differences account for 12 of the strongest peaks in the spectrum (see Table 3 for a listing of the peaks). The 801 cm^{-1} frequency difference has the additional feature of a four-peak progression occurring at 35 652 cm^{-1} (280.49 nm), 34 853 cm^{-1} (286.93 nm), 34 054 cm^{-1} (293.65 mm), and 33 254 cm^{-1} (300.72 nm). Furthermore, a frequency difference of 1599 cm^{-1} is observed and is mostly made up of weak- and medium-intensity peaks, suggesting it might be an overtone of 801 cm^{-1}. This suggests that this frequency is a fundamental mode of O_4^*, and could either be the ν_3 O—O stretch or ν_4 ring deformation mode calculated by Schaefer and co-workers.[4] No such 'overtone' was found for the 437 cm^{-1} frequency.

Closer examination of the frequency differences in Table 2 reveals some relations among these frequencies. The 1639 cm^{-1} frequency, for example, can be obtained within

Table 2 Commonly occurring frequency differences in the O_4^* REMPI spectrum

frequency/cm^{-1}	repetitions
312 ± 1	18
329 ± 1	22
340 ± 1	18
382 ± 1	18
386 ± 1	20
404 ± 1	22
411 ± 1	22
437 ± 1	24
447 ± 1	20
497 ± 1	18
537 ± 1	18
633 ± 1	18
732 ± 1	18
801 ± 1	24
816 ± 1	24
836 ± 1	18
941 ± 1	20
1159 ± 1	22
1599 ± 1	22
1639 ± 1	22
1813 ± 1	18
1954 ± 1	22

Table 3 Frequencies and wavelengths of the most often repeated frequency differences

$\Delta\nu/cm^{-1}$	frequency/cm^{-1}		wavelength/nm	
437	34 792	34 355	287.42	291.08
	34 145	33 709	292.87	296.66
	33 244	32 807	300.81	304.81
	32 680	32 247	307.57	311.75
	32 487	32 048	307.82	312.03
	32 088	31 653	311.64	315.93
	31 726	31 288	315.20	319.61
	31 430	30 992	318.17	322.66
	31 369	30 933	318.79	323.38
	31 244	30 807	320.06	324.60
	31 221	30 783	320.30	324.85
801	35 783	34 982	279.46	285.86
	35 652	34 853	280.49	286.92
	35 144	34 343	284.54	291.18
	34 944	34 145	286.17	292.87
	34 853	34 054	286.95	293.65
	34 054	33 254	293.65	300.72
	32 088	31 288	311.64	319.61
	32 077	31 278	311.75	319.71
	31 861	31 061	313.86	321.95
	31 430	30 628	318.17	326.50
	31 411	30 612	318.36	326.67

error limits from a sum of the 801 cm^{-1} and 835 cm^{-1} frequencies. Similarly, the sum of the 329 cm^{-1} and 403 cm^{-1} frequencies gives 732 cm^{-1}, 339 cm^{-1} and 497 cm^{-1} gives 836 cm^{-1}, 403 cm^{-1} and 410 cm^{-1} gives 816 cm^{-1} and the 941 cm^{-1} frequency can be obtained by adding 403 cm^{-1} and 536 cm^{-1}. Of course, any one of these 'combinations' could also indicate a difference band, *i.e.*, 1639 cm^{-1} could be a fundamental frequency, producing 801 cm^{-1} by subtraction of 835 cm^{-1}. Again, without further studies the experimental vibrational frequencies of O_4^* remain an open question.

Perhaps the most important feature of the spectrum is a proliferation of frequency separations in the 411–419 cm^{-1} range. The 411 ± 1 cm^{-1} difference is listed in Table 2 since it met the criterion of a minimum of 18 recurrences; however, there are 12 recurrences of a 415 ± 1 cm^{-1} and 16 recurrences of a 419 ± 1 cm^{-1} difference. The 415 cm^{-1} difference is especially striking as it corresponds to the difference of the two very intense peaks at 302.13 nm and 305.96 nm and at 284.03 nm and 287.42 nm. This frequency range is also very close to the predicted[3] value of the *c*-O_4 ν_5 pucker mode and the observed range could be the result of anharmonicity. If this is indeed a fundamental mode, the D_{2d} geometry is essentially confirmed, as the smallest frequency expected for a D_{3h} structure should be greater than 495 cm^{-1}, the out-of-plane bending vibration of planar SO_3.[14]

The mechanism of formation of the molecule is of course a matter of speculation, but it is likely that the discharge produces a critical combination of a plasma rich in excited O_2 molecules and rapid supersonic cooling. Although the evidence for this O_4^* as Lewis' cyclic molecule is certainly incomplete at this stage, this remains the most plausible explanation for the observations. Other experiments currently underway include direct VUV probing of the beam, photoelectron spectroscopy and two color spectroscopy experiments. These should provide a more complete picture of the properties of this interesting molecule.

Conclusions

We have produced and directly detected a metastable state of tetraoxygen both by means of a dc discharge and by photodissociation of ozone in the collision region of a molecular beam. We have determined the detection to proceed through a (1 + 1)REMPI process, and have recorded the O_4^* spectrum from 278 to 327 nm. The O_4^* produces a complex spectrum from which general conclusions may be made about the structure of O_4^*. A predominance of peak frequency differences in the range 411–419 cm^{-1} supports a D_{2d} geometry, as predicted by Adamantides *et al.*[4] and Schaefer and co-workers.[3] Other commonly occurring differences compare well with this assignment, although a definitive judgement on the structure of O_4^* awaits further study, which we are pursuing.

H.M.B. acknowledges valuable discussions with Prof. R. Bartlett, Dr R. Copeland, Dr C. Dressler, Prof. Y. T. Lee and Prof. J. Lombardi. This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the US Department of Energy under Contract no. DE-AC03-76SF00098.

References

1 G. N. Lewis, *J. Am. Chem. Soc.*, 1924, **46**, 2027.
2 R. E. Leckenby and E. J. Robbins, *Proc. R. Soc. London A*, 1965, **265**, 389.
3 (*a*) E. T. Seidl and H. F. Schaefer, *J. Chem. Phys.*, 1988, **88**, 7043; (*b*) K. M. Dunn, G. E. Scuseria and H. F. Schaefer, *J. Chem. Phys.*, 1990, **92**, 6077; (*c*) E. T. Seidl and H. F. Schaefer, *J. Chem. Phys.*, 1992, **96**, 1176.
4 (*a*) V. Adamantides, D. Neisius and G. Verhaegen, *Chem. Phys.*, 1980, **48**, 215; (*b*) V. Adamantides, *Chem. Phys.*, 1980, **48**, 221.
5 I. Røegen and E. W. Nilssen, *Chem. Phys. Lett.*, 1989, **157**, 409.
6 M. Hotokka and P. Pyykkö, *Chem. Phys. Lett.*, 1989, **157**, 415.
7 E. Ferreira, P. Gardiol, R. M. Sosa and O. N. Ventura, *J. Mol. Struct.*, 1995, **335**, 63. Note added in proof: recent high level calculations find the D_{3h} form at *ca.* 4.2 eV, A. Korkin, M. Nooijen, J. D. Watts and R. J. Bartlett, unpublished work.
8 R. Lindh and L. A. Barnes, *J. Chem. Phys.*, 1994, **100**, 224.
9 H. Helm and C. W. Walter, *J. Chem. Phys.*, 1993, **98**, 5444.
10 (*a*) C. R. Sherwood, M. C. Garner, K. A. Hanold, K. M. Strong and R. E. Continetti, *J. Chem. Phys.*, 1995, **102**, 6949; (*b*) K. A. Hanold, M. C. Garner and R. E. Continetti, *Phys. Rev. Lett.*, 1996, **77**, 3335.
11 C. L. Lugez, W. E. Thompson and M. E. Jacox, *J. Chem. Phys.*, 1996, **105**, 2153.
12 D. Proch and T. Trickl, *Rev. Sci. Instrum.*, 1989, **60**, 713.
13 D. C. Harris and M. D. Bertolucci, *Symmetry and Spectroscopy*, Dover, New York, 1989.
14 V. E. Bondybey and J. H. English, *J. Mol. Spectrosc.*, 1985, **109**, 221.

Paper 7/05535H; *Received* 30*th July*, 1997